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Nonlinear atomic susceptibilities

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Abstract. Starting with well known formulae for *n*th-order atomic susceptibilities, irreducible spherical tensor techniques and Racah algebra are used to put these in a form suitable for the treatment of complex nonlinear processes, e.g. where fine and hyperfine interactions can be included and the interacting fields can have quite general polarizations. By way of illustration the susceptibilities are calculated in detail for third harmonic generation and Raman scattering in alkali vapours, taking into account the effect of spin–orbit coupling.

1. Introduction

Interest in the nonlinear properties of atomic vapours has increased considerably with the demonstration of their device potential as frequency converters. Possible applications include ultraviolet generation by harmonic generation (Ward and New 1969, Miles and Harris 1973, Leung *et al* 1974), sum frequency generation (Hodgson *et al* 1974), up conversion of infrared radiation (Harris and Bloom 1974), and generation of infrared radiation by four-photon parametric mixing and stimulated Raman scattering (Sorokin *et al* 1973, Sorokin and Lankard 1973, Rokni and Yatsiv 1967, Carlsten and Dunn 1975, Cotter *et al* 1975). Other nonlinear processes of interest include self-focusing (Lehmberg *et al* 1974) and multiphoton absorption and emission (Barak *et al* 1969, Bebb 1966). The exact calculation of the various susceptibilities for these processes can be a tedious exercise. A number of simplifications are usually introduced to keep the calculations down to a reasonable length, for example the assumption that all the interacting waves are plane polarized. Often the fine structure is neglected (although see Bebb 1966, Vriens 1974 and Eicher 1975). Since many of the proposed applications involve interactions which are resonantly enhanced by tuning one or more frequencies close to a resonance transition, it is not always a good approximation to neglect this fine structure. Also, the use of circularly polarized waves can be valuable in suppressing unwanted processes (Hodgson *et al* 1974).

The aim of this paper is therefore to present some rather general susceptibility expressions in which these simplifying assumptions are avoided as far as possible. The main restriction placed on this analysis is to confine the treatment to electric-dipole interactions. Otherwise, however, the expressions apply to any order of susceptibility, to any polarization of the interacting fields, and include the effects of fine structure.

In §2 the notation for the susceptibilities is established beginning with the expression for the *n*th-order nonlinear susceptibility as given by Butcher (1965). To keep this expression in compact form, no damping is included but damping terms can be introduced quite simply into later expressions. The susceptibility formulae contain products of matrix elements of the dipole operator $\boldsymbol{Q} = e\boldsymbol{r}$, of the form $\langle \gamma JM | \boldsymbol{Q} | \gamma' J' M' \rangle$ which connect the initial and final atomic states through a chain of intermediate ('virtual') states.

In §3 we use Racah algebra to sum over the intermediate-state M values. The susceptibility can then be factorized into two parts, in one of which the relation between the fields is explicitly displayed; the other contains the physics of the atom in the form of reduced matrix elements and $6j$ symbols. The magnitude of the reduced matrix element can then be related to oscillator strengths and hence to tabulated experimental data. Once the coupling mode (for example LS or jj) is assumed, the reduced matrix element can be expressed in terms of radial matrix elements. The sign of the radial integral (and hence of the reduced matrix elements) can then be found by calculation.

Finally, the use of these susceptibility expressions is illustrated in §§4 and 5 with a detailed treatment of third harmonic generation and Raman scattering in alkali vapours including the effects of spin–orbit coupling.

2. Nonlinear polarization

We take as our starting point the nth-order nonlinear susceptibility for a loss-free medium of identical, stationary, non-interacting atoms as derived by Butcher (1965) (see also Ducuing (1969) for an alternative derivation), viz:

$$\chi^{(n)}_{\mu\alpha_1\cdots\alpha_n}(-\omega_0;\omega_1\cdots\omega_n) = \frac{(-1)^n N}{n!\,\hbar^n\epsilon_0}\,\mathbf{S}_{\mathrm{T}} \sum_{ab_1\cdots b_n} \rho^0_{aa} \frac{\langle a|Q_\mu|b_1\rangle\langle b_1|Q_{\alpha_1}|b_2\rangle\cdots\langle b_n|Q_{\alpha_n}|a\rangle}{D(ab_1\cdots b_n;\omega_1\cdots\omega_n)} \tag{1}$$

where

$$D(ab_1\cdots b_n;\omega_1\cdots\omega_n) = (\Omega_{ab_1}+\omega_1+\omega_2+\cdots+\omega_n)(\Omega_{ab_2}+\omega_2+\omega_3+\cdots+\omega_n)\cdots \cdots(\Omega_{ab_n}+\omega_n). \tag{2}$$

Here N is the density of atoms, Q_{α_i} is the α_ith Cartesian component of the electric-dipole operator $\boldsymbol{Q} \equiv e\boldsymbol{r}$, Ω_{ab} is the frequency difference of two unperturbed energy levels E_a, E_b of an atom

$$\Omega_{ab} = (E_a - E_b)/\hbar \tag{3}$$

and $\omega_0 = -(\omega_1 + \cdots + \omega_n)$. $\mathbf{S}_{\mathrm{T}}$ is the overall permutation operator which indicates that the expression following it is to be summed over all permutations of the pairs $\mu\omega_0, \alpha_1\omega_1, \ldots, \alpha_n\omega_n$. ρ^0_{aa} is the equilibrium probability distribution for state $|a\rangle$.

The real electric field at frequency ω is written as

$$\boldsymbol{E}(\omega,\boldsymbol{r},t) = \tfrac{1}{2}(\boldsymbol{\epsilon}E_\omega(\boldsymbol{r})\,\mathrm{e}^{-\mathrm{i}\omega t} + \boldsymbol{\epsilon}^* E_{-\omega}(\boldsymbol{r})\,\mathrm{e}^{\mathrm{i}\omega t}), \qquad E^*_\omega(\boldsymbol{r}) = E_{-\omega}(\boldsymbol{r}) \tag{4}$$

where in general the unit magnitude polarization vector $\boldsymbol{\epsilon}$ is a complex linear combination of the real Cartesian unit vectors $\boldsymbol{e}_i$, $(\mathrm{i} \in x, y, z)$. In a similar manner the polarization $\boldsymbol{P}$ at frequency ω_0 can be written as

$$\boldsymbol{P}(\omega_0,\boldsymbol{r},t) = \tfrac{1}{2}(\boldsymbol{\epsilon}_0 P_{\omega_0}(\boldsymbol{r})\,\mathrm{e}^{-\mathrm{i}\omega_0 t} + \boldsymbol{\epsilon}^*_0 P_{-\omega_0}(\boldsymbol{r})\,\mathrm{e}^{\mathrm{i}\omega_0 t}), \qquad P^*_{\omega_0}(\boldsymbol{r}) = P_{-\omega_0}(\boldsymbol{r}). \tag{5}$$

To make full use of tensor techniques it will be necessary to write the polarization vectors $\boldsymbol{\epsilon}$ in terms of the unit complex spherical vectors $\boldsymbol{e}_q$, $(q \in 0, \pm 1)$, instead of the real unit cartesian vectors e_i, ($i \in x, y, z$). The spherical vectors are defined by

$$e_0 = e_z \tag{6a}$$

$$e_{\pm 1} = \mp(e_x \pm \mathrm{i}e_y)/\sqrt{2}. \tag{6b}$$

Notice that

$$e_q^* = -e_{-q}. \tag{7}$$

If we assume an $\mathrm{e}^{\pm \mathrm{i}kz}$ dependence in $E_{\pm\omega}$, then left and right circularly polarized waves propagating in the z direction have fields $\boldsymbol{E}_{+1}$ and $\boldsymbol{E}_{-1}$ respectively, where

$$\boldsymbol{E}_q = \tfrac{1}{2}(e_q E_\omega \mathrm{e}^{-\mathrm{i}\omega t} + e_q^* E_{-\omega}\mathrm{e}^{\mathrm{i}\omega t}), \qquad q = \pm 1 \tag{8}$$

and where $E_{\pm\omega}$ are defined in (4). This may be seen by putting $E_\omega = A\mathrm{e}^{-\mathrm{i}(\phi - kz)}$ (A, ϕ real) and using (6) and (7) in (8). Then for example,

$$\boldsymbol{E}_{+1} = -A[e_x \cos(\omega t - kz + \phi) + e_y \sin(\omega t - kz + \phi)]$$

which can be seen to be left circularly polarized. Notice that a wave linearly polarized in the x direction has its field given by

$$\boldsymbol{E}_x = (\boldsymbol{E}_{-1} - \boldsymbol{E}_{+1})/\sqrt{2}. \tag{9}$$

The importance of using $\boldsymbol{\epsilon}$ or $\boldsymbol{\epsilon}^*$ is now clear—a right circularly polarized beam of positive frequency propagating in the z direction has polarization vector $\boldsymbol{\epsilon} = e_{-1}$, but if of negative frequency it has a polarization vector $\boldsymbol{\epsilon}^* = (e_{-1})^* = -e_{+1}$; yet e_{+1} for a positive frequency describes left circularly polarized light. We consider propagation in an arbitrary direction in §5. It is assumed in such a case that $\boldsymbol{E}_{\pm\omega}(\boldsymbol{r}) \propto \mathrm{e}^{\pm \mathrm{i}\boldsymbol{k}.\boldsymbol{r}}$.

If damping terms are included in the susceptibility expression the susceptibility no longer exhibits overall permutation symmetry as in (1). However from very general considerations (see for example Butcher 1965) it is possible to show that the nth-order susceptibility still possesses intrinsic permutation symmetry, i.e. it is invariant under all permutations of the pairs $\alpha_1\omega_1, \ldots, \alpha_n\omega_n$. This property may be used with definitions (4) and (5) to show that the nth-order polarization at frequency ω_0 has μth component

$$\begin{aligned}(\boldsymbol{\epsilon}_0)_\mu P^{(n)}_{\omega_0}(\boldsymbol{r}) &\equiv P^{(n)}_{\mu,\omega_0}(\boldsymbol{r}) \\ &= \epsilon_0 K(-\omega_0;\omega_1\cdots\omega_n) \sum_{\alpha_1\cdots\alpha_n} \chi^{(n)}_{\mu\alpha_1\cdots\alpha_n}(-\omega_0;\omega_1\cdots\omega_n) E_{\alpha_1\omega_1}(\boldsymbol{r})\cdots E_{\alpha_n\omega_n}(\boldsymbol{r}).\end{aligned} \tag{10}$$

the three Cartesian components $P^{(n)}_{\substack{x\\y\\z}\,\omega_0}(\underline{r})$ would be found by calc. $P^{(n)}_{\omega_0}(r)$ with $\underline{\epsilon_0}$ in the directions x, y, z respectively)

($\mu, \alpha_1\cdots\alpha_n$ are Cartesian components and we use SI units throughout this paper).

The function $K(-\omega_0;\omega_1\cdots\omega_n)$ was introduced by Ward and New (1969) and has been tabulated for $n = 2$ and 3 by Orr and Ward (1971); it contains the factors of $\frac{1}{2}$ from (4) and (5) and the number $\mathscr{D}$ of distinguishable permutations of the frequencies $\omega_1\cdots\omega_n$. If there are no zero frequencies involved,

$$K(-\omega_0;\omega_1\cdots\omega_n) = 2^{1-n}\mathscr{D}. \tag{11}$$

From (4), (5) and (10), and using $\boldsymbol{\epsilon}_0^*.\boldsymbol{\epsilon}_0 = 1$ it is clear that

$$P^{(n)}_{\omega_0}(\boldsymbol{r}) = \epsilon_0 K(-\omega_0;\omega_1\cdots\omega_n)\chi^{(n)}(-\omega_0;\omega_1\cdots\omega_n)E_{\omega_1}(\boldsymbol{r})\cdots E_{\omega_n}(\boldsymbol{r}) \tag{12}$$

where

$$\chi^{(n)}(-\omega_0;\omega_1\cdots\omega_n) \equiv \frac{(-1)^n N}{n!\,\hbar^n\epsilon_0}\mathbf{S}_{\mathrm{T}}\sum_{ab_1\cdots b_n}\rho^0_{aa}\frac{\langle a|\boldsymbol{\epsilon}_0^*.\boldsymbol{Q}|b_1\rangle\langle b_1|\boldsymbol{\epsilon}_1.\boldsymbol{Q}|b_2\rangle\cdots\langle b_n|\boldsymbol{\epsilon}_n.\boldsymbol{Q}|a\rangle}{D(ab_1\cdots b_n;\omega_1\cdots\omega_n)}. \tag{13}$$

In this last equation the overall permutation operator now refers to the pairs $\boldsymbol{\epsilon}_0^*\omega_0, \boldsymbol{\epsilon}_1\omega_1$, etc.

It should be noticed that the $\{\omega_i\}$ in (12) can be negative; thus for example, in the Raman effect where we have a pump field at frequency ω_{p} and a scattered field at frequency ω_{s}, (12) contains $E_{\omega_{\mathrm{p}}}(\boldsymbol{r})$, $E_{-\omega_{\mathrm{p}}}(\boldsymbol{r})$ and $E_{\omega_{\mathrm{s}}}(\boldsymbol{r})$. In such cases (13) should contain $\boldsymbol{\epsilon}_i^*$ corresponding to $E_{-\omega_i}(\boldsymbol{r})$ in (12). Equation (12) may be regarded as a scalarized form of (10) and this was the reason for the choice of notation $\chi^{(n)}(-\omega_0;\omega_1\cdots\omega_n)$, a symbol with no subscripts.

Now it can be shown from Maxwell's equations that the power input to unit volume of the medium from the field at frequency ω_0 is given by the imaginary part of $\frac{1}{2}\omega_0\boldsymbol{\epsilon}^*.\boldsymbol{\epsilon}_0 E_{-\omega_0}(\boldsymbol{r})P_{\omega_0}(\boldsymbol{r})$. Thus since $\chi^{(n)}(-\omega_0;\omega_1\cdots\omega_n)$ as defined in (13) is purely real it cannot be used as it stands to describe non-parametric processes such as the Raman effect, or indeed any resonant process in which absorption of electromagnetic energy by the medium occurs. We therefore follow the usual practice of inserting, by inspection, damping terms of appropriate sign in resonant denominators (see for example Butcher (1965), Ducuing (1969) and Orr and Ward (1971)). As discussed above this must remove the overall (but not the intrinsic) permutation symmetry.

Particular cases of (13) which will be examined in detail later are for third harmonic generation (THG) and two-photon non-parametric processes, viz the stimulated Raman effect (SRE) and two-photon absorption (TPA) and emission (TPE).

For THG, (13) gives

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = \frac{N}{\hbar^3\epsilon_0}\sum_a \rho^0_{aa}\mathscr{M}_{\mathrm{THG}} \equiv \frac{N}{\hbar^3\epsilon_0}\overline{\mathscr{M}_{\mathrm{THG}}} \tag{14}$$

with

$$\begin{aligned}\mathscr{M}_{\mathrm{THG}} = \sum_{bcd} & \frac{\langle a|\boldsymbol{\epsilon}_3^*.\boldsymbol{Q}|b\rangle\langle b|\boldsymbol{\epsilon}.\boldsymbol{Q}|c\rangle\langle c|\boldsymbol{\epsilon}.\boldsymbol{Q}|d\rangle\langle d|\boldsymbol{\epsilon}.\boldsymbol{Q}|a\rangle}{(\Omega_{ba}-3\omega)(\Omega_{ca}-2\omega)(\Omega_{da}-\omega)} \\ & + \frac{\langle a|\boldsymbol{\epsilon}.\boldsymbol{Q}|b\rangle\langle b|\boldsymbol{\epsilon}_3^*.\boldsymbol{Q}|c\rangle\langle c|\boldsymbol{\epsilon}.\boldsymbol{Q}|d\rangle\langle d|\boldsymbol{\epsilon}.\boldsymbol{Q}|a\rangle}{(\Omega_{ba}+\omega)(\Omega_{ca}-2\omega)(\Omega_{da}-\omega)} \\ & + \frac{\langle a|\boldsymbol{\epsilon}.\boldsymbol{Q}|b\rangle\langle b|\boldsymbol{\epsilon}.\boldsymbol{Q}|c\rangle\langle c|\boldsymbol{\epsilon}_3^*.\boldsymbol{Q}|d\rangle\langle d|\boldsymbol{\epsilon}.\boldsymbol{Q}|a\rangle}{(\Omega_{ba}+\omega)(\Omega_{ca}+2\omega)(\Omega_{da}-\omega)} \\ & + \frac{\langle a|\boldsymbol{\epsilon}.\boldsymbol{Q}|b\rangle\langle b|\boldsymbol{\epsilon}.\boldsymbol{Q}|c\rangle\langle c|\boldsymbol{\epsilon}.\boldsymbol{Q}|d\rangle\langle d|\boldsymbol{\epsilon}_3^*.\boldsymbol{Q}|a\rangle}{(\Omega_{ba}+\omega)(\Omega_{ca}+2\omega)(\Omega_{da}+3\omega)},\end{aligned} \tag{15}$$

where the bar over $\mathscr{M}_{\mathrm{THG}}$ denotes the average over initial states made by $\Sigma_a\rho^0_{aa}$. If all the fields are linearly polarized in the z direction (14) and (15) together reduce immediately to the expression for the third harmonic susceptibility given by Miles and Harris (1973).

The Raman susceptibility is obtained from (13) by assuming that the pump field of frequency ω_{p} and polarization vector $\boldsymbol{\epsilon}_{\mathrm{p}}$, and the scattered light of frequency ω_{s} and polarization vector $\boldsymbol{\epsilon}_{\mathrm{s}}$, are in strong resonance with two (possibly degenerate) energy levels, $\hbar\Omega_a$ and $\hbar\Omega_c$, of the medium. Thus $\omega_{\mathrm{p}} - \omega_{\mathrm{s}} \simeq \Omega_{ca}$, where for definiteness we assume $\Omega_c > \Omega_a$. Then it is found that the susceptibility can be expressed in a factorized form (Butcher (1965) considers the non-degenerate case):

$$\chi^{(3)}(-\omega_s;\omega_p,-\omega_p,\omega_s) = \frac{N}{6\hbar^3\epsilon_0}\frac{1}{(\Omega_{ca}+\omega_s-\omega_p)+\mathrm{i}\,\Gamma_{ca}}\sum_{\text{deg of } a}\sum_{\text{deg of } c}(\bar{\rho}^0_{aa}-\bar{\rho}^0_{cc})|\mathscr{M}_{\mathrm{SRE}}|^2 \tag{16}$$

where

$$\mathscr{M}_{\mathrm{SRE}} \equiv \sum_b\left(\frac{\langle c|\boldsymbol{\epsilon}^*_s.\boldsymbol{Q}\,|b\rangle\langle b|\boldsymbol{\epsilon}_p.\boldsymbol{Q}\,|a\rangle}{\Omega_{ba}-\omega_p}+\frac{\langle c|\boldsymbol{\epsilon}_p.\boldsymbol{Q}\,|b\rangle\langle b|\boldsymbol{\epsilon}^*_s.\boldsymbol{Q}\,|a\rangle}{\Omega_{ba}+\omega_s}\right). \tag{17}$$

Γ_{ca} is the phenomenological damping term introduced for reasons discussed above. The sums $\Sigma_{\text{deg of } a}$, $\Sigma_{\text{deg of } c}$ are taken over the degenerate states of energy $\hbar\Omega_a$, $\hbar\Omega_c$ respectively, and $\bar{\rho}^0_{aa}$, $\bar{\rho}^0_{cc}$ are used to indicate the fractional populations of the degenerate states of these energies. It can be seen that (16) takes into account all transitions between the lower and upper levels which contribute to the resonant susceptibility. For the remainder of this paper it will be assumed that degenerate states of a given energy are equally populated.

To obtain the equations for TPA and TPE one merely makes the substitution in (16) and (17) of

$$\boldsymbol{\epsilon}^*_s \to \boldsymbol{\epsilon}_s, \qquad \omega_s \to -\omega_s \qquad \text{and} \qquad \Gamma_{ca} \to -\Gamma_{ca}. \tag{18}$$

The notation $\mathscr{M}_{\mathrm{THG}}$, etc, has been borrowed from Loudon (1973), where these processes are described using a transition rate approach; the results of this paper can thus be applied to his formulae and similar ones. With the transition rate approach one usually assumes a definite initial energy level which for TPE would be level c, so that one has $\rho^0_{aa} = 0$, $\rho^0_{cc} = 1$. The transition rate calculation then leads to the result that $|\mathscr{M}_{\mathrm{TPE}}|^2 = |\mathscr{M}^*_{\mathrm{TPA}}|^2$. Since the expression for $\mathscr{M}^*_{\mathrm{TPA}}$ contains $\boldsymbol{\epsilon}^*_p$, $\boldsymbol{\epsilon}^*_s$, which are associated with $-\omega_p$, $-\omega_s$ in (4), it can be seen that this implies emission of photons at frequencies ω_p and ω_s. However, since $|\mathscr{M}^*_{\mathrm{TPA}}|^2 = |\mathscr{M}_{\mathrm{TPA}}|^2$ we can use $|\mathscr{M}_{\mathrm{TPA}}|^2$ for both TPA and TPE; which of these two processes actually dominates is governed by the sign of the population difference $\bar{\rho}^0_{aa} - \bar{\rho}^0_{cc}$ in (the more general) (16).

3. Reduction of general nonlinear susceptibility

3.1. Recoupling of polarization vectors and summation over intermediate-state degeneracies

Using electric-dipole matrix elements of the form $\langle\gamma JM|\,\boldsymbol{Q}\,|\gamma' J' M'\rangle$ where the symbols have their usual meanings, we consider the function W defined by

$$\begin{aligned} &W(\boldsymbol{\epsilon}_1,\ldots,\boldsymbol{\epsilon}_n;\gamma_1 J_1\cdots\gamma_n J_n \gamma J) \\ &\quad\equiv \sum_{M_2\cdots M_n}\langle\gamma_1 J_1 M_1|\boldsymbol{\epsilon}_1.\boldsymbol{Q}\,|\gamma_2 J_2 M_2\rangle\langle\gamma_2 J_2 M_2|\boldsymbol{\epsilon}_2.\boldsymbol{Q}\,|\gamma_3 J_3 M_3\rangle\cdots \\ &\quad\quad\cdots\langle\gamma_n J_n M_n|\boldsymbol{\epsilon}_n.\boldsymbol{Q}\,|\gamma JM\rangle. \end{aligned} \tag{19}$$

The 'initial state', $|\gamma JM\rangle$, is referred to by not using a suffix; if J_{n+1} occurs we write J instead, and similarly for γ_{n+1}, M_{n+1}. By permuting all the $\boldsymbol{\epsilon}_i$ in (19) and dividing by the appropriate frequency factors one clearly recovers the 'matrix elements' $\mathscr{M}$ discussed above.

For the remainder of this paper we use the notations and conventions of Brink and Satchler (1971) (BS) and Shore and Menzel (1968) (SM). (Caution should be exercised in using formulae from the latter reference as the book contains a number of typographical errors.) It should be noted however that these works differ in their definition of reduced matrix element, and we have adopted the choice in SM. The reduced matrix element of SM is $(2J + 1)^{1/2}$ times the corresponding reduced matrix element as defined by BS.

Tensor products will be written as

$$\begin{aligned} T_Q^{(K)}(\boldsymbol{A}^{(k)} \times \boldsymbol{B}^{(k')}) &\equiv (\boldsymbol{A}^{(k)} \times \boldsymbol{B}^{(k')})_Q^{(K)} \equiv (k \times k')_Q^{(K)} \\ &= (2K + 1)^{1/2}(-1)^{k-k'+Q} \sum_{q_1 q_2} \begin{pmatrix} k & k' & K \\ q_1 & q_2 & -Q \end{pmatrix} A_{q_1}^{(k)} B_{q_2}^{(k')} \end{aligned} \qquad (20)$$

where we use a $3j$ symbol in preference to a Clebsch–Gordan coefficient. For brevity we shall use the notation $[x, y, \ldots] \equiv [(2x + 1)(2y + 1)\cdots]$. Using (20) it is seen that the dot product of two tensors is

$$\boldsymbol{T}^{(K)} \cdot \boldsymbol{U}^{(K)} \equiv \sum_Q (-1)^Q T_{-Q}^{(K)} U_Q^{(K)} = (-1)^K [K]^{1/2} (\boldsymbol{T}^{(K)} \times \boldsymbol{U}^{(K)})_0^{(0)}. \qquad (21)$$

With these preliminaries we return to (19). In appendix 1 it is shown, using (21), as a basis, that the generalization of the vector relations

$$\boldsymbol{a}_1 \cdot \boldsymbol{b}_1 = \boldsymbol{b}_1 \cdot \boldsymbol{a}_1$$

$$\boldsymbol{a}_1 \cdot \boldsymbol{b}_1 \boldsymbol{a}_2 \cdot \boldsymbol{b}_2 = \tfrac{1}{3} \boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \boldsymbol{b}_1 \cdot \boldsymbol{b}_2 + \tfrac{1}{2}(\boldsymbol{a}_1 \times \boldsymbol{a}_2) \cdot (\boldsymbol{b}_1 \times \boldsymbol{b}_2) + (\boldsymbol{a}_1 \times \boldsymbol{a}_2)^{(2)} \cdot (\boldsymbol{b}_1 \times \boldsymbol{b}_2)^{(2)}$$

(BS p 149) to nth-order is

$$\begin{aligned} &\boldsymbol{a}_1 \cdot \boldsymbol{b}_1 \boldsymbol{a}_2 \cdot \boldsymbol{b}_2 \cdots \boldsymbol{a}_n \cdot \boldsymbol{b}_n \\ &\quad = \sum_{K_2 \cdots K_n} (-1)^{K_n + n} (\cdots((\boldsymbol{a}_1 \times \boldsymbol{a}_2)^{(K_2)} \times \boldsymbol{a}_3)^{(K_3)} \cdots \times \boldsymbol{a}_n)^{(K_n)} \\ &\quad\quad \cdot (\cdots((\boldsymbol{b}_1 \times \boldsymbol{b}_2)^{(K_2)} \times \boldsymbol{b}_3)^{(K_3)} \cdots \times \boldsymbol{b}_n)^{(K_n)}. \end{aligned} \qquad (22)$$

The superscripts $^{(1)}$ on the vectors have not been included as the meaning is clear.

By identifying $\boldsymbol{a}_j$ with $\boldsymbol{\epsilon}_j$ and $\boldsymbol{b}_j$ with $\langle \gamma_j J_j M_j | \boldsymbol{Q} | \gamma_{j+1} J_{j+1} M_{j+1} \rangle$ it is seen that the fields have been separated from the medium as represented by matrix elements. Reference to the discussion in appendix 3 shows that this is the basic step in reducing (1) to spherical tensor form.

Using graphical techniques for clarity it is shown in appendix 2 that

$$\begin{aligned} &\sum_{M_2 \cdots M_n} (\cdots(\langle \gamma_1 J_1 M_1 | \boldsymbol{Q} | \gamma_2 J_2 M_2 \rangle \times \langle \gamma_2 J_2 M_2 | \boldsymbol{Q} | \gamma_3 J_3 M_3 \rangle)^{(K_2)} \times \cdots \\ &\qquad \times \langle \gamma_n J_n M_n | \boldsymbol{Q} | \gamma J M \rangle)_{Q_n}^{(K_n)} \\ &\quad = (-1)^{J_1 - M_1 + P_n} [K_2, K_3 \cdots K_n]^{1/2} \langle \gamma_1 J_1 \| \boldsymbol{Q} \| \gamma_2 J_2 \rangle \langle \gamma_2 J_2 \| \boldsymbol{Q} \| \gamma_3 J_3 \rangle \cdots \\ &\qquad \cdots \langle \gamma_n J_n \| \boldsymbol{Q} \| \gamma J \rangle \begin{pmatrix} J_1 & K_n & J \\ -M_1 & Q_n & M \end{pmatrix} \begin{Bmatrix} J_1 & K_2 & J_3 \\ 1 & J_2 & 1 \end{Bmatrix} \begin{Bmatrix} J_1 & K_3 & J_4 \\ 1 & J_3 & K_2 \end{Bmatrix} \cdots \\ &\qquad \cdots \begin{Bmatrix} J_1 & K_{l-1} & J_l \\ 1 & J_{l-1} & K_{l-2} \end{Bmatrix} \cdots \begin{Bmatrix} J_1 & K_n & J \\ 1 & J_n & K_{n-1} \end{Bmatrix} \end{aligned} \qquad (23)$$

where

$$\begin{aligned} P_n = (J_1 + K_2 + J_3) + (J_1 + K_3 + J_4) + \cdots + (J_1 + K_{l-1} + J_l) + \cdots \\ + (J_1 + K_n + J). \end{aligned} \qquad (24)$$

The phase factor P_n is just the sum of the top lines of the $6j$ symbols that appear in (23).

The angular momenta $J_1, J_2, \ldots, J_n, J$ of the states determine, through triangle and integer rules in the $6j$ symbols, the allowed values of $K_2 \cdots K_n$. The physics of particular atoms is contained in the reduced matrix elements and thus the dependence on field polarization vectors for processes in atomic gases and vapours can be determined with no reference to LS, jj or other coupling modes.

Combining (22) and (23) with the use of (21) we obtain

$$\begin{aligned} &W(\boldsymbol{\epsilon}_1 \cdots \boldsymbol{\epsilon}_n; \gamma_1 J_1, \ldots, \gamma_n J_n, \gamma J) \\ &\quad = \sum_{Q_n, K_2 \cdots K_n} (-1)^{J_1 - M_1 + P_n + K_n + Q_n + n} [K_2, \ldots, K_n]^{1/2} \\ &\quad \times \langle \gamma_1 J_1 \| \boldsymbol{Q} \| \gamma_2 J_2 \rangle \cdots \langle \gamma_n J_n \| \boldsymbol{Q} \| \gamma J \rangle \, T^{(K_n)}_{-Q_n} \begin{pmatrix} J_1 & K_n & J \\ -M_1 & Q^n & M \end{pmatrix} \\ &\quad \times \begin{Bmatrix} J_1 & K_2 & J_3 \\ 1 & J_2 & 1 \end{Bmatrix} \begin{Bmatrix} J_1 & K_3 & J_4 \\ 1 & J_3 & K_2 \end{Bmatrix} \cdots \begin{Bmatrix} J_1 & K_n & J \\ 1 & J_n & K_{n-1} \end{Bmatrix} \end{aligned} \tag{25}$$

where

$$T^{(K_n)}_{-Q_n} \equiv (\cdots((\boldsymbol{\epsilon}_1 \times \boldsymbol{\epsilon}_2)^{(K_2)} \times \boldsymbol{\epsilon}_3)^{(K_3)} \times \cdots \times \boldsymbol{\epsilon}_n)^{(K_n)}_{-Q_n}. \tag{26}$$

While it might appear that (25) merely replaces the sum over $M_2 \cdots M_n$ by another, that over $K_2 \cdots K_n$, it should be realized that in general the latter sum is far more restricted; furthermore it has the advantage of the insight given by the separation of the fields from the matrix elements; this is discussed more fully below.

It is well known that a tensor of odd rank describing a polar property of a medium with inversion symmetry vanishes identically. This can be seen clearly in (13) applied to a gas of atoms. Here, as the atomic wavefunctions have definite parity and electric-dipole transitions are considered, there must be $n + 1$ changes of parity as we go through the states $|a\rangle$, $|b_1\rangle \cdots |b_n\rangle$, $|a\rangle$. The first and last states are the same, $|a\rangle$, so they have the same parity, and thus as parity is two-valued $n + 1$ must be even, i.e. the tensor must be of even rank. For the rest of this paper n is therefore taken to be odd.

This property is a consequence of the inversion symmetry of a single atom. The average over degenerate states implied by $\Sigma_a \rho^0_{aa}$ in (3) introduces the macroscopic isotropy of the medium. Writing

$$\sum_a \rho^0_{aa} = \sum_{\gamma J} \rho^0_{\gamma J - \gamma J} \frac{1}{[J]} \sum_{M=-J}^{J} \tag{27}$$

(13) and (19) can be combined to give

$$\begin{aligned} &\chi^{(n)}(-\omega_0; \omega_1 \cdots \omega_n) \\ &\quad = \frac{(-1)^n N}{n! \, \hbar^n \epsilon_0} \mathbf{S}_{\mathrm{T}} \sum_{\gamma J} \rho^0_{\gamma J - \gamma J} \frac{1}{[J]} \\ &\quad \times \sum_{M=-J}^{J} \sum_{\gamma_1 J_1 \cdots \gamma_n J_n} \frac{W(\boldsymbol{\epsilon}_0^*, \boldsymbol{\epsilon}_1, \ldots, \boldsymbol{\epsilon}_n; \gamma J, \gamma_1 J_1, \ldots, \gamma_n J_n, \gamma J)}{D(\gamma J, \gamma_1 J_1 \cdots \gamma_n J_n; \omega_1, \ldots, \omega_n)}. \end{aligned} \tag{28}$$

We have had to go to $n + 1$ matrix elements and renumber the labels in (19) on passing to (28) so that $\boldsymbol{\epsilon}_1 \cdots \boldsymbol{\epsilon}_{n+1} \rightarrow \boldsymbol{\epsilon}_0^*, \boldsymbol{\epsilon}_1 \cdots \boldsymbol{\epsilon}_n$ and $\gamma_1 J_1 \cdots \gamma_{n+1} J_{n+1}, \gamma J \rightarrow \gamma J, \gamma_1 J_1 \cdots \gamma_n J_n, \gamma J$. Then using this relabelling in the explicit form of W given in (25), it is clear that the average $\mathscr{A}$ given by

$$\mathscr{A} \equiv \frac{1}{[J]} \sum_{M=-J}^{J} (-1)^{J-M} \begin{pmatrix} J & K_{n+1} & J \\ -M & Q_{n+1} & M \end{pmatrix} \tag{29}$$

needs to be evaluated. The 3j selection rule gives $Q_{n+1} = 0$. It can be shown in several ways (for example by explicit reduction and summation of the formula for the 3j symbols) that

$$\mathscr{A} = \frac{1}{[J]^{1/2}} \delta_{K_{n+1},0}\, \delta_{Q_{n+1},0}. \tag{30}$$

From the 6j selection rules $K_{n+1} = 0$ implies $K_n = 1$. After a little tidying up, we finally have

$$\begin{aligned} &\chi^{(n)}(+\omega_0;\omega_1\cdots\omega_n) \\ &\quad = \frac{-N}{n!\,\hbar^n\epsilon_0} \mathbf{S}_\mathrm{T} \sum_{\gamma J,\gamma_1 J_1\cdots\gamma_n J_n} \sum_{K_2\cdots K_{n-1}} (-1)^{2J+\phi_{n-1}} \rho^0_{\gamma J-\gamma J}[J]^{-1} \\ &\qquad \times [K_2\cdots K_{n-1}]^{1/2} \langle\gamma J\|\boldsymbol{Q}\|\gamma_1 J_1\rangle\cdots\langle\gamma_n J_n\|\boldsymbol{Q}\|\gamma J\rangle \\ &\qquad \times \frac{((\cdots((\boldsymbol{\epsilon}_0^* \times \boldsymbol{\epsilon}_1)^{(K_2)} \times \boldsymbol{\epsilon}_2)^{(K_3)} \times \cdots \times \boldsymbol{\epsilon}_{n-1})^{(1)} \times \boldsymbol{\epsilon}_n)_0^{(0)}}{D(\gamma J,\gamma_1 J_1\cdots\gamma_n J_n;\omega_1\cdots\omega_n)} \begin{Bmatrix} J & K_2 & J_2 \\ 1 & J_1 & 1 \end{Bmatrix} \\ &\qquad \times \begin{Bmatrix} J & K_3 & J_3 \\ 1 & J_2 & K_2 \end{Bmatrix} \cdots \begin{Bmatrix} J & K_{n-1} & J_{n-1} \\ 1 & J_{n-2} & K_{n-1} \end{Bmatrix} \begin{Bmatrix} J & 1 & J_n \\ 1 & J_{n-1} & K_{n-1} \end{Bmatrix} \end{aligned} \tag{31a}$$

where

$$\phi_{n-1} = (J + K_2 + J_2) + (J + K_3 + J_3) + \cdots + (J + K_{n-1} + J_{n-1}). \tag{31b}$$

This is the simplest working formula for the nth-order nonlinear susceptibility. From this equation we can write down at once as detailed an atomic structure as is required for describing a particular process. The fact that $K_{n+1} = 0$ is not a coincidence. It can be deduced as a consequence of symmetry by the use of group theory, and this is shown in appendix 3. It is also shown in this appendix that (31) represents the reduction of the susceptibility tensor to irreducible spherical form, where $K_2\cdots K_{n-1}$ label different spherical tensors. Reference to (31) shows another physical interpretation of the $K_2\cdots K_{n+1}(=0)$. This is that K_l is the total angular momentum of l coupled electric fields. Thus $\boldsymbol{\epsilon}_0^*$ is a tensor of rank one, transforming as a field having an angular momentum of one. Two fields $\boldsymbol{\epsilon}_0^*$, $\boldsymbol{\epsilon}_1$ can couple to give a total angular momentum of 0, 1 or 2. In making a dipole transition from $|\gamma_{l-1}J_{l-1}\rangle$ to $|\gamma_l J_l\rangle$ we use a field of angular momentum one, and so get the triangle rule from the 6j symbols on 1, J_l and J_{l-1}. But in getting to the state $|\gamma_l J_l\rangle$, l dipole transitions have been made from the state $|\gamma J\rangle$ to $|\gamma_1 J_1\rangle$ and then to $|\gamma_2 J_2\rangle$ up to $|\gamma_l J_l\rangle$, and so have involved l fields of total angular momentum K_l. Hence the 6j symbols contain a triangle rule on K_l, J and J_l.

3.2. *Calculation of reduced matrix elements*

In equation (31) it can be seen that the physics of the atoms is expressed in the form of reduced matrix elements. It is customary to obtain the values of the reduced matrix elements from experimental data, through the relationship to electric-dipole oscillator strength:

$$\langle\gamma J\|\boldsymbol{Q}\|\gamma' J'\rangle^2 = \frac{3\hbar e^2}{2m} [J] \frac{f_{\gamma J-\gamma' J'}}{\Omega_{\gamma' J'-\gamma J}}. \tag{32}$$

The sign of the reduced matrix element may be found by assuming a particular coupling mode and then writing it in terms of radial integrals. The signs of the integrals (and hence of the reduced matrix elements) are then obtained from theoretical calculations where available. Vriens (1974) has used a combination of experimental and theoretical results to deduce these signs for indium and thallium. In view of the considerable interest in alkali vapours we give the reduction using *LS* coupling for one electron:

$$\begin{aligned}\langle\gamma J\|\boldsymbol{Q}\|\gamma' J'\rangle &= \langle nlsJ\|\boldsymbol{Q}\|n'l'sJ'\rangle\\ &= [J,J']^{1/2}(-1)^{l+J'+\frac{3}{2}}\begin{Bmatrix}1 & J & J'\\ \frac{1}{2} & l' & l\end{Bmatrix}\langle nl\|\boldsymbol{Q}\|n'l'\rangle \qquad (33)\end{aligned}$$

(see for example SM p 299). Here s is of course $\frac{1}{2}$. Using the notation $l_>$ to mean the greater of l and l' we find, using (SM p 298)

$$\langle nl\|\boldsymbol{Q}\|n'l'\rangle = e(-1)^{l_>-l}\sqrt{l_>}\,\langle nl|r|n'l'\rangle \qquad (34)$$

and (33) that

$$\langle\gamma J\|\boldsymbol{Q}\|\gamma' J'\rangle = e([J,J']l_>)^{1/2}(-1)^{l_>+J'+\frac{3}{2}}\begin{Bmatrix}1 & J & J'\\ \frac{1}{2} & l' & l\end{Bmatrix}\langle nl|r|n'l'\rangle. \qquad (35)$$

The radial matrix element may be related to the $\mathscr{R}_{nl;n'l'}$ used by Miles and Harris (1973):

$$\langle nl|r|n'l'\rangle = (4l_>^2-1)^{1/2}\mathscr{R}_{nl;n'l'} = \frac{(4l_>^2-1)^{1/2}}{l_>}\langle nl0|z|n'l'0\rangle. \qquad (36)$$

The state $|nl0\rangle$ is a hydrogenic orbital $|nlm_l = 0\rangle$. As tabulations of $\langle nl|r|n'l'\rangle$ are available for the alkalis (see for example Miles and Harris 1973, Eicher 1975) we shall use the coupling (35) in the examples of §§4 and 5, rather than leave the results in terms of reduced matrix elements.

4. Third harmonic generation in alkali vapours

From (15) and (31) we may immediately write

$$\begin{aligned}\overline{\mathscr{M}_{\mathrm{THG}}} = \sum_{\gamma J\gamma_1 J_1\gamma_2 J_2\gamma_3 J_3}\sum_{K_2}\frac{1}{[J]}\rho^0_{\gamma J-\gamma J}(-1)^{J+K_2+J_2}[K_2]^{1/2}&\begin{Bmatrix}J & K_2 & J_2\\ 1 & J_1 & 1\end{Bmatrix}\begin{Bmatrix}J & 1 & J_3\\ 1 & J_2 & K_2\end{Bmatrix}\\ \times\langle\gamma J\|\boldsymbol{Q}\|\gamma_1 J_1\rangle\langle\gamma_1 J_1\|\boldsymbol{Q}\|\gamma_2 J_2\rangle&\langle\gamma_2 J_2\|\boldsymbol{Q}\|\gamma_3 J_3\rangle\\ \times\langle\gamma_3 J_3\|\boldsymbol{Q}\|\gamma J\rangle F(K_2)& \qquad (37)\end{aligned}$$

where

$$\begin{aligned}F(K_2) \equiv{}& \frac{(((\boldsymbol{\epsilon}_3^*\times\boldsymbol{\epsilon})^{(K_2)}\times\boldsymbol{\epsilon})^{(1)}\times\boldsymbol{\epsilon})^{(0)}_0}{(\Omega_{\gamma_1 J_1\gamma J}-3\omega)(\Omega_{\gamma_2 J_2\gamma J}-2\omega)(\Omega_{\gamma_3 J_3\gamma J}-\omega)}\\ &+\frac{(((\boldsymbol{\epsilon}\times\boldsymbol{\epsilon}_3^*)^{(K_2)}\times\boldsymbol{\epsilon})^{(1)}\times\boldsymbol{\epsilon})^{(0)}_0}{(\Omega_{\gamma_1 J_1\gamma J}+\omega)(\Omega_{\gamma_2 J_2\gamma J}-2\omega)(\Omega_{\gamma_3 J_3\gamma J}-\omega)}\\ &+\frac{(((\boldsymbol{\epsilon}\times\boldsymbol{\epsilon})^{(K_2)}\times\boldsymbol{\epsilon}_3^*)^{(1)}\times\boldsymbol{\epsilon})^{(0)}_0}{(\Omega_{\gamma_1 J_1\gamma J}+\omega)(\Omega_{\gamma_2 J_2\gamma J}+2\omega)(\Omega_{\gamma_3 J_3\gamma J}-\omega)}\\ &+\frac{(((\boldsymbol{\epsilon}\times\boldsymbol{\epsilon})^{(K_2)}\times\boldsymbol{\epsilon})^{(1)}\times\boldsymbol{\epsilon}_3^*)^{(0)}_0}{(\Omega_{\gamma_1 J_1\gamma J}+\omega)(\Omega_{\gamma_2 J_2\gamma J}+2\omega)(\Omega_{\gamma_3 J_3\gamma J}+3\omega)}. \qquad (38)\end{aligned}$$

Study of the polarization vector coupling soon reveals that $F(K_2 = 1) = 0$, and so only the cases $K_2 = 0$ and 2 need be considered. It is an easy matter to retain this coupling in the examples below; however, since experimentally it is usual to use collinearly propagating linearly polarized light, we restrict the analysis to this case and put $\boldsymbol{\epsilon} = \boldsymbol{\epsilon}_3^* = \boldsymbol{e}_0$. (If the vector coupling is kept it soon becomes clear that $\overline{\mathscr{M}_{\mathrm{THG}}}$ vanishes if $\boldsymbol{\epsilon}$ is circularly polarized; this is a well known result.) Assuming linearly polarized light and defining a frequency factor

$$\mathscr{F}(\gamma_1 J_1 \gamma_2 J_2 \gamma_3 J_3) \equiv F(K_2) \text{ with numerators put equal to unity,} \tag{39}$$

it is soon found with the aid of (20) that

$$F(0) = \tfrac{1}{3}\mathscr{F}(\gamma_1 J_1 \gamma_2 J_2 \gamma_3 J_3) \tag{40a}$$

and

$$F(2) = \frac{2}{3\sqrt{5}}\mathscr{F}(\gamma_1 J_1 \gamma_2 J_2 \gamma_3 J_3). \tag{40b}$$

4.1. Alkali atom with no spin–orbit coupling

As an example we start with the simple case of a gas of alkali atoms all in the ground state, neglecting fine structure. The state labels used are $|\gamma' J'\rangle = |n'l'\rangle$ where it is understood that the spin is $s = \frac{1}{2}$ for all states. As the ground state is $|n\mathrm{s}\rangle$, the $6j$ selection rules imply $J_1 \equiv l_1 = 1\ (\equiv \mathrm{p}) = J_3 \equiv l_3$ and $J_2 \equiv l_2 = 0$ or 2 (s or d). This is a manifestation of the well known electric-dipole selection rule. Using (34) and (40), (37) becomes, after the simple task of evaluating the $6j$ symbols,

$$\begin{aligned}\overline{\mathscr{M}_{\mathrm{THG}}} = \frac{e^4}{9} \sum_{n_1 n_2 n_3} &\langle n\mathrm{s}|\, r\,|n_1\mathrm{p}\rangle\, (\langle n_1\mathrm{p}|\, r\,|n_2\mathrm{s}\rangle \langle n_2\mathrm{s}|\, r\,|n_3\mathrm{p}\rangle\, \mathscr{F}(n_1\mathrm{p}, n_2\mathrm{s}, n_3\mathrm{p}) \\ &+ \tfrac{4}{5}\langle n_1\mathrm{p}|\, r\,|n_2\,\mathrm{d}\rangle\, \langle n_2\,\mathrm{d}|\, r\,|n_3\mathrm{p}\rangle \mathscr{F}(n_1\mathrm{p}, n_2\,\mathrm{d}, n_3\mathrm{p}))\, \langle n_3\mathrm{p}|\, r\,|n\mathrm{s}\rangle.\end{aligned} \tag{41}$$

Application of (36) to (41) gives the expression used by Miles and Harris (1973).

4.2. Alkali atom with spin–orbit coupling

The ground state is now $|n^2\mathrm{S}_{1/2}\rangle$, and we use state labels $|\gamma' J'\rangle = |n'l'\tfrac{1}{2}J'\rangle$ where the $\frac{1}{2}$ refers to spin. Again $l_1 = l_3 = 1$, and $l_2 = 0$ or 2, but now there are 9 possible intermediate state $l'J'$ choices, with $K_2 = 0$ or 2 to take into account. Enumeration of the possibilities (of which there are less than 18 due to limitations on J', K_2 imposed by the $6j$ symbols) and using (35) for the reduced matrix elements leads directly to

$$\begin{aligned}\overline{\mathscr{M}_{\mathrm{THG}}} = \frac{e^4}{81} \sum_{n_1 n_2 n_3} &\langle n\mathrm{s}|\, r\,|n_1\mathrm{p}\rangle \langle n_1\mathrm{p}|\, r\,|n_2\mathrm{s}\rangle \langle n_2\mathrm{s}|\, r\,|n_3\mathrm{p}\rangle \langle n_3\mathrm{p}|\, r\,|n\mathrm{s}\rangle \\ &\times (\mathscr{F}(n_1\mathrm{p}\tfrac{1}{2}, n_2\mathrm{s}\tfrac{1}{2}, n_3\mathrm{p}\tfrac{1}{2}) + 2\mathscr{F}(n_1\mathrm{p}\tfrac{1}{2}, n_2\mathrm{s}\tfrac{1}{2}, n_3\mathrm{p}\tfrac{3}{2}) + 2\mathscr{F}(n_1\mathrm{p}\tfrac{3}{2}, n_2\mathrm{s}\tfrac{1}{2}, n_3\mathrm{p}\tfrac{1}{2}) \\ &+ 4\mathscr{F}(n_1\mathrm{p}\tfrac{3}{2}, n_2\mathrm{s}\tfrac{1}{2}, n_3\mathrm{p}\tfrac{3}{2})) + \frac{2e^4}{81} \sum_{n_1 n_2 n_3} \langle n\mathrm{s}|\, r\,|n_1\mathrm{p}\rangle \langle n_1\mathrm{p}|\, r\,|n_2\mathrm{d}\rangle \\ &\times \langle n_2\mathrm{d}|\, r\,|n_3\mathrm{p}\rangle \langle n_3\mathrm{p}|\, r\,|n\mathrm{s}\rangle (\mathscr{F}(n_1\mathrm{p}\tfrac{1}{2}, n_2\mathrm{d}\tfrac{3}{2}, n_3\mathrm{p}\tfrac{1}{2}) \\ &+ \tfrac{1}{5}\mathscr{F}(n_1\mathrm{p}\tfrac{1}{2}, n_2\mathrm{d}\tfrac{3}{2}, n_3\mathrm{p}\tfrac{3}{2}) + \tfrac{1}{5}\mathscr{F}(n_1\mathrm{p}\tfrac{3}{2}, n_2\mathrm{d}\tfrac{3}{2}, n_3\mathrm{p}\tfrac{1}{2}) \\ &+ \tfrac{1}{25}\mathscr{F}(n_1\mathrm{p}\tfrac{3}{2}, n_2\mathrm{d}\tfrac{3}{2}, n_3\mathrm{p}\tfrac{3}{2}) + \tfrac{54}{25}\mathscr{F}(n_1\mathrm{p}\tfrac{3}{2}, n_2\mathrm{d}\tfrac{5}{2}, n_3\mathrm{p}\tfrac{3}{2})).\end{aligned} \tag{42}$$

(We have not used a label for spin in the frequency factors as this is unnecessary; the argument reads $\mathscr{F}(n_1l_1J_1, n_2l_2J_2, n_3l_3J_3)$.) If the coupling is now 'turned off', each frequency factor with $l_2 = \mathrm{s}$ becomes the $\mathscr{F}(n_1\mathrm{p}, n_2\mathrm{s}, n_3\mathrm{p})$ of (41), and similarly for $l_2 = \mathrm{d}$. Adding up the result leads back to (41) as expected.

From (37) and (38) it can be seen that it is only necessary to alter the frequency factors in (42) to obtain the susceptibility for four-wave mixing.

5. The Raman effect

An *ab initio* treatment of Raman scattering can start directly from (31) in the same way as already illustrated for the case of THG. However since it is possible to put the expression for the Raman susceptibility in a factorized form as in (16) we shall start with this form and use (25) directly. Unlike the treatment of THG given above, we retain the general dependence on polarization vectors since the angular scattering distribution of Stokes radiation is of experimental importance.

From (16), (17) and (25) we find, if all the atoms are in the lower state so that $\bar{\rho}^0_{aa} = [J]^{-1}$ and $\bar{\rho}^0_{cc} = 0$,

$$\sum_{\text{deg of } a}\ \sum_{\text{deg of } c} \bar{\rho}^0_{aa} |\mathscr{M}_{\mathrm{SRE}}|^2 \equiv \overline{|\mathscr{M}_{\mathrm{SRE}}|^2}$$

$$= \frac{1}{[J]} \sum_{M,M_1} \left| \sum_{\gamma_2 J_2} \sum_{KQ} (-1)^Q [K]^{1/2} \begin{pmatrix} J_1 & K & J \\ -M_1 & Q & M \end{pmatrix} \right.$$

$$\times \begin{Bmatrix} J_1 & K & J \\ 1 & J_2 & 1 \end{Bmatrix} \langle \gamma_1 J_1 \| \boldsymbol{Q} \| \gamma_2 J_2 \rangle \langle \gamma_2 J_2 \| \boldsymbol{Q} \| \gamma J \rangle$$

$$\left. \times \left(\frac{(\boldsymbol{\epsilon}^*_{\mathrm{s}} \times \boldsymbol{\epsilon}_{\mathrm{p}})^{(K)}_{-Q}}{(\Omega_{\gamma_2 J_2 \gamma J} - \omega_{\mathrm{p}})} + \frac{(\boldsymbol{\epsilon}_{\mathrm{p}} \times \boldsymbol{\epsilon}^*_{\mathrm{s}})^{(K)}_{-Q}}{(\Omega_{\gamma_2 J_2 \gamma J} + \omega_{\mathrm{s}})} \right) \right|^2 . \tag{43}$$

(Use has been made of the square modulus to remove most of the phase, and the subscript on K_2, Q_2 omitted as it no longer serves any purpose.)

Now the nth-order tensor coupled fields do not in general admit of simple permutation properties; however, for two such vectors we have the result from (20) that

$$(\boldsymbol{\epsilon}^*_{\mathrm{s}} \times \boldsymbol{\epsilon}_{\mathrm{p}})^{(K)} = (-1)^K (\boldsymbol{\epsilon}_{\mathrm{p}} \times \boldsymbol{\epsilon}^*_{\mathrm{s}})^{(K)}. \tag{44}$$

The $3j$ symbol can be eliminated from (43) as follows. Considering (43) in the form

$$\sum_{M,M_1} \left| \sum_K \sum_Q (-1)^Q \begin{pmatrix} J_1 & K & J \\ -M_1 & Q & M \end{pmatrix} [K]^{1/2} (\boldsymbol{\epsilon}^*_{\mathrm{s}} \times \boldsymbol{\epsilon}_{\mathrm{p}})^{(K)}_{-Q} \phi(K, \omega_{\mathrm{p}}, \omega_{\mathrm{s}}, \gamma J, \gamma_1 J_1) \right|^2 ,$$

in which (44) has been used, the square modulus may be expanded by multiplying out the terms in the sum over K. Then the sum over M, M_1 may be carried out by using the $3j$ symbol orthogonality relationship

$$\sum_{M,M_1} \begin{pmatrix} J & J_1 & K \\ M & -M_1 & Q \end{pmatrix} \begin{pmatrix} J & J_1 & K' \\ M & -M_1 & Q' \end{pmatrix} = \frac{1}{[K]} \delta_{K,K'} \delta_{Q,Q'} . \tag{45}$$

This removes the cross terms and leaves

$$\overline{|\mathscr{M}_{\mathrm{SRE}}|^2} = \frac{1}{[J]} \sum_K \left| \sum_{\gamma_2 J_2} \begin{Bmatrix} J_1 & K & J \\ 1 & J_2 & 1 \end{Bmatrix} \langle \gamma_1 J_1 \| \boldsymbol{Q} \| \gamma_2 J_2 \rangle \langle \gamma_2 J_2 \| \boldsymbol{Q} \| \gamma J \rangle \right.$$

$$\left. \times \left(\frac{1}{(\Omega_{\gamma_2 J_2 \gamma J} - \omega_{\mathrm{p}})} + \frac{(-1)^K}{(\Omega_{\gamma_2 J_2 \gamma J} + \omega_{\mathrm{s}})} \right) \right|^2 \Theta^{(K)} \tag{46}$$

where the angular dependence is contained in the factor

$$\Theta^{(K)} = \sum_{Q} |(\boldsymbol{\epsilon}_{\mathrm{s}}^{*} \times \boldsymbol{\epsilon}_{\mathrm{p}})_{Q}^{(K)}|^{2}. \tag{47}$$

Equation (46) applies for any atom, provided the total angular momenta J_i remain good quantum numbers. It is shown in appendix 3, using arguments based purely on the symmetry of an isotropic medium, that any process described by a third-order nonlinear susceptibility can only have an angular dependence on the fields involved given by linear combinations of

$$(((\boldsymbol{\epsilon}_{0}^{*} \times \boldsymbol{\epsilon}_{1})^{(K)} \times \boldsymbol{\epsilon}_{2})^{(1)} \times \boldsymbol{\epsilon}_{3})_{0}^{(0)} \tag{48a}$$

(see (A.3.4)) which may be shown with the aid of (20) to be equal to

$$\frac{(-1)^{K}}{[K]^{1/2}} (\boldsymbol{\epsilon}_{0}^{*} \times \boldsymbol{\epsilon}_{1})^{(K)}.(\boldsymbol{\epsilon}_{2} \times \boldsymbol{\epsilon}_{3})^{(K)} \qquad (K = 0, 1 \text{ or } 2). \tag{48b}$$

Then for the Raman effect in any isotropic medium, we put $\boldsymbol{\epsilon}_0 = \boldsymbol{\epsilon}_2 = \boldsymbol{\epsilon}_{\mathrm{s}}$, $\boldsymbol{\epsilon}_1 = \boldsymbol{\epsilon}_3^{*} = \boldsymbol{\epsilon}_{\mathrm{p}}$ (this follows from the expanded form of (16) and (17), as discussed above) and find that (48) is equal to $\Theta^{(K)}/[K]^{1/2}$, again by use of (20).

Thus although the particular examples discussed below are concerned with alkali atoms, the results for $\Theta^{(K)}$ apply to any isotropic medium, for example a molecular gas or liquid. The study of the angular distribution of Stokes radiation from such media is of interest since it can yield information about the symmetries of the initial and final molecular states involved (see for example Damen *et al* 1965).

For the remainder of this section we will deal with hydrogenic atoms, and it is convenient to introduce the definition

$$\Phi(n_2 l_2 J_2 K) \equiv \langle n_1 l_1 | r | n_2 l_2 \rangle \langle n_2 l_2 | r | nl \rangle \left(\frac{1}{(\Omega_{n_2 l_2 J_2 nlJ} - \omega_{\mathrm{p}})} + \frac{(-1)^{K}}{(\Omega_{n_2 l_2 J_2 nlJ} + \omega_{\mathrm{s}})} \right). \tag{49}$$

Then (46) becomes

$$\overline{|\mathscr{M}_{\mathrm{SRE}}|^{2}} = \frac{1}{[J]} \sum_{K} \left| \sum_{n_2 l_2 J_2} \begin{Bmatrix} J_1 & K & J \\ 1 & J_2 & 1 \end{Bmatrix} \Phi(n_2 l_2 J_2 K) \right.$$
$$\left. \times \frac{\langle n_1 l_1 \tfrac{1}{2} J_1 \| Q \| n_2 l_2 \tfrac{1}{2} J_2 \rangle \langle n_2 l_2 \tfrac{1}{2} J_2 \| Q \| nl \tfrac{1}{2} J \rangle}{\langle n_1 l_1 | r | n_2 l_2 \rangle \langle n_2 l_2 | r | nl \rangle} \right|^{2} \Theta^{(K)} \tag{50}$$

where the $\frac{1}{2}$ refers to spin.

5.1. *Alkali atoms with no spin–orbit coupling*

We put $J_i \rightarrow l_i$; then assuming an $l = 0$ initial state we can only have $l_2 = 1$ and $K = l_1$, as a consequence of the $6j$ symbol selection rules (see §4.1).

Using (35), (50) now becomes

$$\overline{|\mathscr{M}_{\mathrm{SRE}}|^{2}_{\text{Spin-free}}} = \frac{e^{4} l_{>}}{3[l_1]} \left| \sum_{n_2} \Phi(n_2 \mathrm{p}, K = l_1) \right|^{2} \Theta^{(l_1)} \tag{51}$$

where $l_{>}$ in (51) is the greater of $l_2 = 1$ and $l_1 = 0$ or 2. (As $J_i = l_i$, the label l_2 in (49) is redundant here, and so is omitted.)

In order to discuss the dependence on propagation and polarization directions of the pump and Stokes radiation contained in (47), and therefore (51), it is convenient to express $\boldsymbol{\epsilon}_p$ with respect to axes $\boldsymbol{e}_m$ $(m \in 0, \pm 1)$ and to express $\boldsymbol{\epsilon}_s^*$ with respect to axes $\boldsymbol{e}'_n$ $(n \in 0, \pm 1)$ in a rotated frame. Thus

$$\boldsymbol{e}'_n = \sum_m \boldsymbol{e}_m D^{(1)}_{mn}(R) \tag{52}$$

where $\boldsymbol{e}_0$ is chosen as the z axis and R is a proper rotation. Then for cases of greatest practical importance, $\boldsymbol{\epsilon}_p = \boldsymbol{\epsilon}_{q_p}$ in the fixed frame and $\boldsymbol{\epsilon}_s^* = (\boldsymbol{e}'_{q_s})^* = -\boldsymbol{e}'_{-q_s}$ in the rotated frame. Equations (20), (47) and (52) together give

$$\Theta^{(K)} = [K] \sum_Q \left| \sum_q \begin{pmatrix} 1 & 1 & K \\ q & q_p & -Q \end{pmatrix} D^{(1)}_{q,-q_s}(R) \right|^2 \tag{53}$$

i.e.

$$\Theta^{(K)} = [K] \sum_Q \begin{pmatrix} 1 & 1 & K \\ Q - q_p & q_p & -Q \end{pmatrix}^2 (d^{(1)}_{Q-q_p,-q_s}(\beta))^2. \tag{54}$$

In view of (9), to describe linearly polarized light propagating along the positive z axis (in the fixed or rotated frame), one should strictly use for example $\boldsymbol{\epsilon}_p = \boldsymbol{e}_x = (\boldsymbol{e}_{-1} - \boldsymbol{e}_{+1})/\sqrt{2}$. Then (53) would be summed over $q_p = \pm 1$ inside the square modulus. However, it is easier to choose the polarization vectors in this case to lie along the fixed or rotated positive z axis, for then only one angle, β, in (54) is used. The angle β will now vary in physical meaning depending on the polarization vectors involved, but this presents no difficulties.

If both beams are linearly polarized (lp), $q_s = q_p = 0$, and so

$$\Theta^{(0)}_{\text{lp}} = \tfrac{1}{3}\cos^2 \beta_1 \tag{55a}$$

where β_1 is the angle between the polarization vectors. When they are both circularly polarized in the same sense (ss), $q_s = q_p = \pm 1$,

$$\Theta^{(0)}_{\text{ss}} = \tfrac{1}{12}(\cos \beta_2 + 1)^2 \tag{55b}$$

or in opposite senses (os), $-q_s = q_p = \pm 1$,

$$\Theta^{(0)}_{\text{os}} = \tfrac{1}{12}(\cos \beta_2 - 1)^2 \tag{55c}$$

where β_2 is the angle between the directions of propagation of the two beams. Finally, if one beam is linearly and the other circularly polarized (lc)

$$\Theta^{(0)}_{\text{lc}} = \tfrac{1}{6}\sin^2 \beta_3 \tag{55d}$$

where β_3 is the angle between the linear polarization vector and the direction of propagation of the circularly polarized beam.

Returning to (51), $\Theta^{(0)}$ gives the angular distribution when the absorption and emission process leaves the atom in an s state (the same angular momentum as the initial state). Equations (55*b*) and (55*c*) show conservation of angular momentum, as is seen by considering the special case of collinear propagation, $\beta_2 = 0$, when there is no emission of oppositely circularly polarized radiation. This is because the atom has not changed its angular momentum in the Raman transition and so neither can the radiation field. The pump and scattered light must have the same sense of circular polarization or both be linearly polarized for emission with $\beta_2 = 0$. To discuss TPA or TPE one uses (18), so that (55*b*) and (55*c*) need to be interchanged.

Though (51) only allows the intensity distribution to be given by $\Theta^{(0)}$ or $\Theta^{(2)}$, it is convenient at this point to also give the formulae for $\Theta^{(1)}$; then as can be seen by applying the triangle rule to the 6j symbol in (46), these, (55) and (57) below enumerate all the possible angular distributions involved in two-photon and Raman processes.

Accordingly we find

$$\Theta^{(1)}_{\mathrm{lp}} = \tfrac{1}{2}\sin^2\beta_1 \tag{56a}$$

$$\Theta^{(1)}_{\mathrm{ss}} = \tfrac{1}{8}(3 + 2\cos\beta_2 - \cos^2\beta_2) \tag{56b}$$

$$\Theta^{(1)}_{\mathrm{os}} = \tfrac{1}{8}(3 - 2\cos\beta_2 - \cos^2\beta_2) \tag{56c}$$

$$\Theta^{(1)}_{\mathrm{lc}} = \tfrac{1}{4}(\cos^2\beta_3 + 1) \tag{56d}$$

where the notation introduced above has been used.

When in (51) the final state is a d state we require $\Theta^{(2)}$, given by

$$\Theta^{(2)}_{\mathrm{lp}} = \tfrac{1}{6}(3 + \cos^2\beta_1) \tag{57a}$$

$$\Theta^{(2)}_{\mathrm{ss}} = \tfrac{1}{24}(13 - 10\cos\beta_2 + \cos^2\beta_2) \tag{57b}$$

$$\Theta^{(2)}_{\mathrm{os}} = \tfrac{1}{24}(13 + 10\cos\beta_2 + \cos^2\beta_2) \tag{57c}$$

$$\Theta^{(2)}_{\mathrm{lc}} = \tfrac{1}{12}(6 + \sin^2\beta_3) \tag{57d}$$

again with the same notation used above. From (57c) the emission of Stokes radiation circularly polarized in the opposite sense to the pump, leaving the atom in a d state, is a maximum when the beams are propagating collinearly in the positive z direction, $\beta_2 = 0$. This is the opposite to that found when the atom is left in an s state. Physically the reason for this can be seen by considering a two-step absorption and then emission process. Absorption by the atom of a circularly polarized photon prepares it in a p, $m_l = 1$ orbital. Subsequent emission of a photon polarized in the same sense takes the atom to a d, $m_l = 0$ orbital, but if of opposite sense, to d, $m_l = 2$. As is apparent from a consideration of the electron probability distribution in these orbitals, or mathematically by an elementary application of the Wigner–Eckart theorem (in the form given in (A.2.1), appendix 2), $|\mathrm{p}, m_l = 1\rangle$ to $|d, m_l = 2\rangle$ is the stronger transition, in agreement with the result (57c).

It is interesting to note that the $\Theta^{(K)}$ satisfy a normalization,

$$\sum_K \Theta^{(K)} = 1 \tag{58}$$

which is easily verified by adding corresponding terms in equations (55) to (57). Consider an alkali atom with no spin–orbit coupling, with p orbitals as the initial and final states, so that $l = l_1 = 1$, and with the pump frequency strongly resonant with a transition energy Ω_{n_2snp} from the initial state. In this case all other intermediate states, and the anti-resonant part $(-1)^K(\Omega_{n_2snp} + \omega_s)^{-1}$ of $\Phi(n_2, l_2 = 0, K)$, may be ignored, making it independent of K. Further, the 6j symbol in (50) depends on K only through a phase factor which is removed by the square modulus. Hence the angular distribution of scattered radiation is proportional to (58), i.e. is isotropic.

This may be understood easily, because absorption of light of any polarization from the initial p state leaves the atom in a spherically symmetric intermediate virtual state, effectively destroying knowledge of this first beam. Emission of light leaving the atom in a final p state may then be observed equally well for all polarizations.

5.2. *Alkali atom with spin–orbit coupling*

The introduction of spin–orbit (LS) coupling is now only a marginal extra complication. For a comparison with the results of the previous section we consider a $|n^2\mathrm{S}_{1/2}\rangle$ ground state with each of the three possible final states, viz $|n_1^2\mathrm{S}_{1/2}\rangle$, $|n_1^2\mathrm{D}_{3/2}\rangle$ and $|n_1^2\mathrm{D}_{5/2}\rangle$. The details of the calculation for the first case are given, and the results for the other two cases quoted.

From the $6j$ symbol in (50), if $J = J_1 = \frac{1}{2}$ then $J_2 = \frac{1}{2}$ and $\frac{3}{2}$, and $K = 0$ and 1. Using (35) and (50) with $l_1 = l = 0, l_2 = 1$,

$$\begin{aligned}\overline{|\mathscr{M}_{\mathrm{SRE}}|^2_{LS}} = 2e^4 \Bigg| \sum_{n_2} \Bigg[& [\tfrac{1}{2}] \begin{Bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 1 & \frac{1}{2} & 1 \end{Bmatrix} \begin{Bmatrix} 1 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 1 & 0 \end{Bmatrix} \begin{Bmatrix} 1 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & 1 \end{Bmatrix} \Phi(n_2\mathrm{p}\tfrac{1}{2}0) \\ & - [\tfrac{3}{2}] \begin{Bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 1 & \frac{3}{2} & 1 \end{Bmatrix} \begin{Bmatrix} 1 & \frac{1}{2} & \frac{3}{2} \\ \frac{1}{2} & 1 & 0 \end{Bmatrix} \begin{Bmatrix} 1 & \frac{3}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & 1 \end{Bmatrix} \Phi(n_2\mathrm{p}\tfrac{3}{2}0) \Bigg] \Bigg|^2 \Theta^{(0)} \\ & + \text{similar term with } K = 1 \\ = \frac{e^4}{3} & \left| \sum_{n_2} [\tfrac{2}{3}\Phi(n_2\mathrm{p}\tfrac{3}{2}0) + \tfrac{1}{3}\Phi(n_2\mathrm{p}\tfrac{1}{2}0)] \right|^2 \Theta^{(0)} \\ + \frac{2e^4}{81} & \left| \sum_{n_2} [\Phi(n_2\mathrm{p}\tfrac{3}{2}1) - \Phi(n_2\mathrm{p}\tfrac{1}{2}1)] \right|^2 \Theta^{(1)} \qquad (J_1 = \tfrac{1}{2}).\end{aligned} \tag{59}$$

The other results are

$$\overline{|\mathscr{M}_{\mathrm{SRE}}|^2_{LS}} = \frac{2e^4}{25} \left| \sum_{n_2} \Phi(n_2\mathrm{p}\tfrac{3}{2}2) \right|^2 \Theta^{(2)} \qquad (J_1 = \tfrac{5}{2}) \tag{60}$$

and

$$\begin{aligned}\overline{|\mathscr{M}_{\mathrm{SRE}}|^2_{LS}} = & \frac{e^4}{81} \left| \sum_{n_2} [\Phi(n_2\mathrm{p}\tfrac{3}{2}1) - \Phi(n_2\mathrm{p}\tfrac{1}{2}1)] \right|^2 \Theta^{(1)} \\ & + \frac{4e^4}{75} \left| \sum_{n_2} [\tfrac{1}{6}\Phi(n_2\mathrm{p}\tfrac{3}{2}2) + \tfrac{5}{6}\Phi(n_2\mathrm{p}\tfrac{1}{2}2)] \right|^2 \Theta^{(2)} \qquad (J_1 = \tfrac{3}{2}).\end{aligned} \tag{61}$$

Clearly, if the spin–orbit interaction is ‘turned off’, the difference terms vanish and the sum terms coalesce; then (59) reduces to (51) with $l_1 = 0$, and the sum of (60) and (61) reduces to (51) with $l_1 = 2$. When ω_p is away from any energy differences $\Omega_{n_2\mathrm{p}J_2 n\mathrm{s}\frac{1}{2}}$ there is no resonant denominator in $\Phi(n_2\mathrm{p}J_2K)$ so that the difference terms are negligible, and then the angular distributions are similar to the ‘spin-free’ cases considered in §5.1. One is in effect disregarding the doublet splitting of the energy levels. As ω_p approaches a resonance the difference terms cannot be neglected in general and the angular distribution becomes a complicated function of frequency. In the extreme of near exact resonance with one energy level only, there is a contribution from just one term in the sums over n_2 and J_2. The anti-resonant part of $\Phi(n_2\mathrm{p}J_2K)$

can then be dropped and this allows its label K to be omitted. Then for example, if $J_2 = \frac{1}{2}$, (59) approaches

$$\frac{e^4}{27}\left|\Phi(n_2\mathrm{p}\tfrac{1}{2})\right|^2[\Theta^{(0)} + \tfrac{2}{3}\Theta^{(1)}]. \tag{62}$$

When both beams are linearly polarized (55*a*) and (56*a*) give the ratio of the second to the first term in (62) as $\tan^2\beta_1$. When the beams are polarized in the same direction then the second part makes no resonant contribution, and in fact one can see from (56*a*) with $\beta_1 = 0$ that this conclusion remains valid for the exact expression (59). This result applies to TPA since (18) provides the prescription for converting SRE expressions to TPA ones.

As ω_p is tuned between a doublet, it is seen from (59) and (61), for example, that destructive interference occurs and the Raman susceptibility will become extremely small at some point. This has been seen experimentally in the case of TPA in sodium vapour by Bjorkholm and Liao (1974). One would expect the cancellation in the (stimulated) Raman susceptibility to be more difficult to observe experimentally, due to the large gain narrowing of the dip in this case.

When the beams are linearly polarized the existence of spin–orbit coupling means that even if $\beta_1 = \frac{1}{2}\pi$ some emission should still occur, and in the most favourable case, that of resonance, this is only 25% of the usual arrangement where $\beta_1 = 0$, from (62). However in stimulated Raman generation where the Stokes radiation is generated from noise, only that frequency and polarization of emission for which the (exponential) gain is largest will appear at the output—there is a 'gain narrowing' of the angular distributions as given by (55) to (57).

6. Discussion

The results presented in this paper can be viewed in a number of ways. Firstly, a purely algebraic procedure has been used to sum over all the degenerate intermediate states in the nonlinear susceptibility (1), and also to average over the initial- and final-state degeneracies, the first sum being equivalent to an orientational average. The resulting formula, (31), represents the simplest possible form of (1) for a gas of atoms. It contains essentially only reduced matrix elements, which describe the physics of particular atoms, and a separate factor describing the dependence of the macroscopic polarization on field polarization vectors. By starting from (31) rather than (1) one can immediately write down the susceptibility for any nonlinear process in full generality. The more usual procedures, either of explicitly writing out in full, say, the *LS*-coupled wavefunctions using 3*j* or Clebsch–Gordan coefficients, or of using the Wigner–Eckart theorem to get a result more quickly in terms of these same coefficients, are rather tedious. Hence special choices of polarization vectors are usually made to simplify the working. The expression (31) is quicker to use than either of these approaches even without making such restrictions. Clearly in some cases, such as for third harmonic generation with no spin–orbit coupling, this generality is superfluous. The point we wish to emphasize is that even then (31) is just as easy to use as (1). When angular dependences are of importance, as in the Raman effect, then (31) gives the required results very directly.

This is clearer when one considers the discussion in appendix 3. There it has been shown by the use of group theory that the major features of (31) may be predicted on the basis of symmetry, and that this expression is in fact the reduction of (1) to irreducible spherical tensor form. Thus it is to be expected that (31) should contain in the most compact manner all the physics of the atomic susceptibility.

As can be seen from §4, equation (46) for the Raman effect (which can be made to apply to two-photon absorption and emission by use of (18)) leads to the angular dependences on polarization vectors given by (55) to (57). These angular factors follow from the conservation of angular momentum and explicitly display this. They are the two-photon analogues of angular momentum conservation as described in most standard quantum theory texts for single-photon processes.

Appendix 1

The proof of (22) is most simply carried out by using the relation (Soo 1971, equation (8*a*)):

$$((a\times b)^{(e)}\times(c\times d)^{(e)})^{(0)}=\sum_{f}(-1)^{b+c+e+f}[e,f]^{1/2}\begin{Bmatrix}a & b & e\\ d & c & f\end{Bmatrix}((a\times c)^{(f)}\times(b\times d)^{(f)})^{(0)} \qquad \text{(A1.1)}$$

where a, b, c, d represent both tensors and their respective ranks. Using the vectors $\boldsymbol{a}_1\cdots\boldsymbol{a}_n$, $\boldsymbol{b}_1\cdots\boldsymbol{b}_n$, each a tensor of rank one, (21) and (A1.1) give

$$(\boldsymbol{a}_1\times\boldsymbol{b}_1)^{(0)}(\boldsymbol{a}_2\times\boldsymbol{b}_2)^{(0)}=\sum_{K_2}(-1)^{K_2}[K_2]^{1/2}\begin{Bmatrix}1 & 1 & 0\\ 1 & 1 & K_2\end{Bmatrix}((\boldsymbol{a}_1\times\boldsymbol{a}_2)^{(K_2)}\times(\boldsymbol{b}_1\times\boldsymbol{b}_2)^{(K_2)})^{(0)}. \qquad \text{(A1.2)}$$

Assume

$$\begin{aligned}R_n &\equiv(\boldsymbol{a}_1\times\boldsymbol{b}_1)^{(0)}(\boldsymbol{a}_2\times\boldsymbol{b}_2)^{(0)}\cdots(\boldsymbol{a}_n\times\boldsymbol{b}_n)^{(0)}\\ &=(-1)^n\sum_{K_2\cdots K_n}(-1)^{K_n}[K_2,\ldots,K_n]^{1/2}\\ &\quad\times\begin{Bmatrix}1 & 1 & 0\\ 1 & 1 & K_2\end{Bmatrix}\begin{Bmatrix}K_2 & K_2 & 0\\ 1 & 1 & K_3\end{Bmatrix}\cdots\begin{Bmatrix}K_{n-1} & K_{n-1} & 0\\ 1 & 1 & K_n\end{Bmatrix}\\ &\quad\times(((\boldsymbol{a}_1\times\boldsymbol{a}_2)^{(K_2)}\times\cdots\times\boldsymbol{a}_n)^{(K_n)}\times((\boldsymbol{b}_1\times\boldsymbol{b}_2)^{(K_2)}\times\cdots\times\boldsymbol{b}_n)^{(K_n)})^{(0)}. \qquad \text{(A1.3)}\end{aligned}$$

Now by (A1.1),

$$\begin{aligned}&((\boldsymbol{a}_1\times\cdots\times\boldsymbol{a}_n)^{(K_n)}\times(\boldsymbol{b}_1\times\cdots\times\boldsymbol{b}_n)^{(K_n)})^{(0)}(\boldsymbol{a}_{n+1}\times\boldsymbol{b}_{n+1})^{(0)}\\ &\quad=\sum_{K_{n+1}}(-1)^{1+K_n+K_{n+1}}[K_{n+1}]^{1/2}\begin{Bmatrix}K_n & K_n & 0\\ 1 & 1 & K_{n+1}\end{Bmatrix}\\ &\quad\times((\boldsymbol{a}_1\times\cdots\times\boldsymbol{a}_{n+1})^{(K_{n+1})}\times(\boldsymbol{b}_1\times\cdots\times\boldsymbol{b}_{n+1})^{(K_{n+1})})^{(0)}. \qquad \text{(A1.4)}\end{aligned}$$

Substitution of (A1.4) in (A1.3) shows

$$(\boldsymbol{a}_{n+1}\times\boldsymbol{b}_{n+1})^{(0)}R_n=R_{n+1}. \qquad \text{(A1.5)}$$

Hence if R_n is true, R_{n+1} is true, but R_2 is correct by (A1.2), and so (A1.3) is true for all $n \geqslant 2$ by induction.

Using

$$\begin{Bmatrix}a & a & 0\\ b & b & c\end{Bmatrix}=(-1)^{a+b+c}[a,b]^{-1/2} \qquad \text{(A1.6)}$$

and (21) in (A1.3) gives (22) and this completes the proof.

Appendix 2

In this appendix we prove (23) and (24) using graphical techniques. These have been extensively developed in recent years; for the purposes of what follows the material in BS is adequate. An algebraic procedure could have been used, but this is longer and much less clear.

Using the Wigner–Eckart theorem in the form

$$\langle \gamma JM | Q_q | \gamma' J'M' \rangle = (-1)^{J-M} \begin{pmatrix} J & 1 & J' \\ -M & q & M' \end{pmatrix} \langle \gamma J \| \boldsymbol{Q} \| \gamma' J' \rangle \tag{A2.1}$$

and (20) it is seen that

$$\begin{aligned} &\sum_{M_2 \cdots M_n} (\cdots (\langle \gamma_1 J_1 M_1 | \boldsymbol{Q} | \gamma_2 J_2 M_2 \rangle \times \langle \gamma_2 J_2 M_2 | \boldsymbol{Q} | \gamma_3 J_3 M_3 \rangle)^{(K_2)} \times \cdots \\ &\qquad \times \langle \gamma_n J_n M_n | \boldsymbol{Q} | \gamma JM \rangle)^{(K_n)}_{Q_n} \\ &\quad = \sum_{M_2 \cdots M_n} \sum_{m_1 \cdots m_n} \sum_{Q_2 \cdots Q_{n-1}} [K_2, \ldots, K_n]^{1/2} (-1)^{\phi_1 + \phi_2} \langle \gamma_1 J_1 \| \boldsymbol{Q} \| \gamma_2 J_2 \rangle \\ &\qquad \times \langle \gamma_2 J_2 \| \boldsymbol{Q} \| \gamma_3 J_3 \rangle \cdots \langle \gamma_n J_n \| \boldsymbol{Q} \| \gamma J \rangle \begin{pmatrix} J_1 & a_1 & J_2 \\ -M_1 & m_1 & M_2 \end{pmatrix} \\ &\qquad \times \begin{pmatrix} J_2 & a_2 & J_3 \\ -M_2 & m_2 & M_3 \end{pmatrix} \cdots \begin{pmatrix} J_n & a_n & J \\ -M_n & m_n & M \end{pmatrix} \begin{pmatrix} a_1 & a_2 & K_2 \\ m_1 & m_2 & -Q_2 \end{pmatrix} \\ &\qquad \times \begin{pmatrix} K_2 & a_3 & K_3 \\ Q_2 & m_3 & -Q_3 \end{pmatrix} \cdots \begin{pmatrix} K_{n-1} & a_n & K_n \\ Q_{n-1} & m_n & -Q_n \end{pmatrix} \end{aligned} \tag{A2.2a}$$

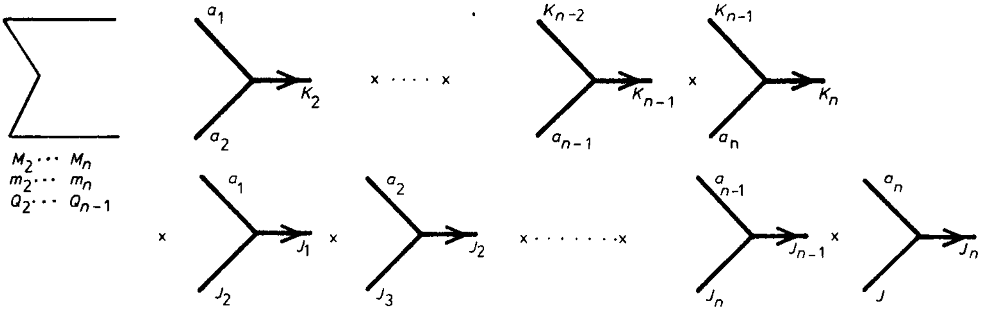
where

$$\begin{aligned} \phi_1 = {} & (J_1 + M_1) + (J_2 + M_2) + \cdots + (J_n + M_n) + (K_2 + Q_2) + (K_3 + Q_3) + \cdots \\ & + (K_n + Q_n) \end{aligned} \tag{A2.2b}$$

and

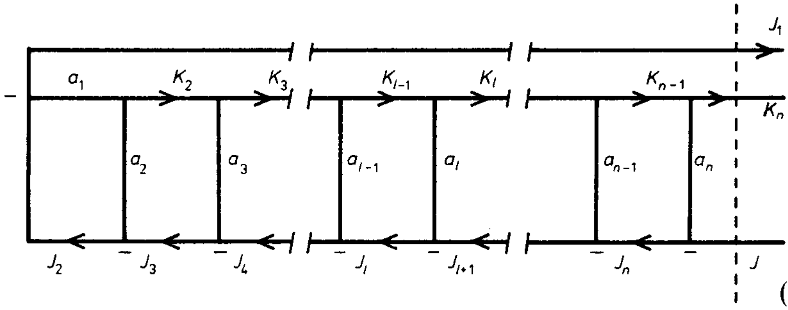
$$\phi_2 = 2(J_1 + J_2 + \cdots + J_n) + K_n + (a_1 + a_2 + \cdots + a_n). \tag{A2.2c}$$

Here the a_i are each numerically equal to one, as they represent the rank of the tensor $\boldsymbol{Q}$. These labels are needed in order to follow the individual symbols in the diagrams below. In these diagrams unmarked nodes are taken as positive. Equation (A2.2a) is, less $(-1)^{\phi_2}[K_2 \cdots K_n]^{1/2}$ and the reduced matrix elements,



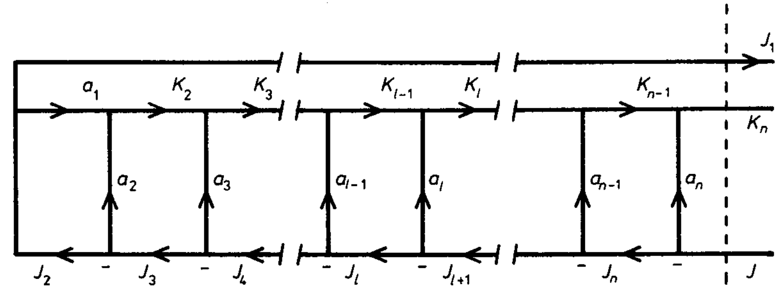
(A2.3)

Performing the sums by joining appropriate lines. (A2.3) may be deformed into



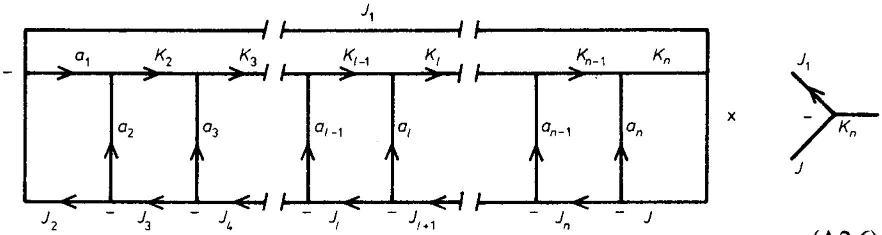
(A2.4)

The part to the left of the dotted line is an invariant as may be seen by drawing three arrows into each unmarked (positive) node in (A2.4):



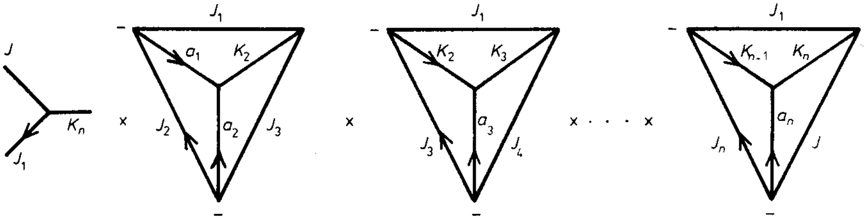
(A2.5)

Thus a $3j$ symbol may be separated off:



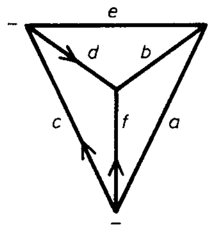
(A2.6)

The invariant can now be split up along the lines (J_1, K_2, J_3), (J_1, K_3, J_4) and so on to give



(A2.7)

Now



$$= (-1)^{-a+d+e+f}\begin{Bmatrix} a & b & e \\ d & c & f \end{Bmatrix} \qquad \text{(A2.8)}$$

Thus from (A2.7) and (A2.8), (A2.2) is

$$[K_2 \cdots K_n]^{1/2} \langle \gamma_1 J_1 \| \boldsymbol{Q} \| \gamma_2 J_2 \rangle \langle \gamma_2 J_2 \| \boldsymbol{Q} \| \gamma_3 J_3 \rangle \cdots \langle \gamma_n J_n \| \boldsymbol{Q} \| \gamma J \rangle (-1)^{J_1 - M_1 + P_n}$$
$$\times \begin{pmatrix} J_1 & K_n & J \\ -M_1 & Q_n & M \end{pmatrix} \begin{Bmatrix} J_1 & K_2 & J_3 \\ 1 & J_2 & 1 \end{Bmatrix} \begin{Bmatrix} J_1 & K_3 & J_4 \\ 1 & J_3 & K_2 \end{Bmatrix} \cdots \begin{Bmatrix} J_1 & K_n & J \\ 1 & J_n & K_{n-1} \end{Bmatrix} \qquad \text{(A2.9)}$$

where

$$P_n = (J_1 + K_2 + J_3) + (J_1 + K_3 + J_4) + \cdots + (J_1 + K_n + J). \qquad \text{(A2.10)}$$

In order to obtain P_n one has to use the $6j$ symbol integer rules extensively, after transcribing (A2.8) to algebraic form, and using (A2.2*c*).

Appendix 3

It is stated in most texts on basic group theory that a Cartesian tensor can be decomposed into irreducible spherical tensors. The actual procedure has been discussed by Coope *et al* (1965), Jerphagnon (1970) and Yuratich (1975, unpublished), but for the purposes of this paper the following is adequate, and deals in particular with the results for isotropic media.

A general nth-order nonlinear electric susceptibility tensor transforms under the full rotation–reflection group R(3) as the direct product of $(n + 1)$ polar vectors,

$$D_-^{(1)}(\mathrm{R}) \times D_-^{(1)}(\mathrm{R}) \times \cdots (n+1) \text{ times} \qquad \text{(A3.1)}$$

for a (possibly improper) rotation R. Here the irreducible representations (IR) of the proper rotation group $\mathrm{R}^+(3)$, $D^{(K)}$, used in the body of this paper, become $D_+^{(K)}$ and $D_-^{(K)}$ for R(3); ($\mathrm{R}(3) = \mathrm{R}^+(3) \times i$ where i is the inversion group). $D_+^{(K)}$ and $D_-^{(K)}$ are respectively even and odd under inversion. The direct product may be decomposed (see for example Tinkham 1964 pp 127, 140):

$$D_-^{(1)} \times D_-^{(1)} = D_+^{(2)} + D_+^{(1)} + D_+^{(0)}$$
$$D_-^{(1)} \times D_-^{(1)} \times D_-^{(1)} = D_-^{(3)} + 2D_-^{(2)} + 3D_-^{(1)} + D_-^{(0)} \qquad \text{(A3.2)}$$
$$D_-^{(1)} \times D_-^{(1)} \times D_-^{(1)} \times D_-^{(1)} = D_+^{(4)} + 3D_+^{(3)} + 6D_+^{(2)} + 6D_+^{(1)} + 3D_+^{(0)}$$

and so on.

The implication of (A3.2) is that linear combinations of the Cartesian tensor components can be found which form irreducible bases for the $D_\pm^{(K)}$. These combinations transform as the components of spherical tensors of rank K. As an example, in the notation used in this paper the third-order nonlinear susceptibility would lead to an expression of the form

$$\boldsymbol{E}_{-\omega_0}.\boldsymbol{P}^{(3)}_{\omega_0} = \sum_{K_2K_3K_4} \epsilon_0\chi(K_2, K_3)^{(K_4)}.(((\boldsymbol{E}_{-\omega_0} \times \boldsymbol{E}_{\omega_1})^{(K_2)} \times \boldsymbol{E}_{\omega_2})^{(K_3)} \times \boldsymbol{E}_{\omega_3})^{(K_4)} \tag{A3.3}$$

where $\boldsymbol{E}_{\omega_i} \equiv \boldsymbol{\epsilon}_i E_{\omega_i}(\boldsymbol{r})$. Here $\chi(K_1, K_3)^{(K_4)}$ is a spherical tensor of rank K_4 transforming as $D^{(K_4)}_+$ and K_2, K_3 label any inequivalent spherical tensors.

Now it is well known (see for example Lax 1974) that the number of independent components in an $(n + 1)$th-rank tensor describing some property of a medium with symmetry group $\mathscr{G}$ is equal to the number of times the identity representation of $\mathscr{G}$ is contained in (A3.1). Consider a medium which is both isotropic and has inversion symmetry i.e. $\mathscr{G} = \mathrm{R}(3)$. The identity is $D^{(0)}_+$ (even under inversion) and so from (A3.2) odd rank tensors (which decompose into IR odd under inversion) vanish and this is thus a consequence of inversion symmetry alone. As the third-order nonlinear susceptibility contains $3D^{(0)}_+$ it has three components. When written in spherical form only the scalar term $\chi(K_2 \cdots K_n)^{(0)}$ of the $(n + 1)$th-rank tensor is non-zero, as $D^{(0)}_+$ is, by definition, not in $D^{(1)}_+$, $D^{(2)}_+$, etc. Thus $K_{n+1} \equiv 0$, and

$$\boldsymbol{E}_{-\omega_0}.\boldsymbol{P}^{(n)}_{\omega_0} = \sum_{K_2\cdots K_{n-1}} \epsilon_0\chi(K_2 \cdots K_{n-1}, K_n \equiv 1)^{(0)}_0(\cdots(\boldsymbol{E}_{-\omega_0} \times \boldsymbol{E}_{\omega_1})^{(K_2)} \times \cdots \times \boldsymbol{E}_{\omega_n})^{(0)}_0. \tag{A3.4}$$

This result is completely general for an isotropic medium. Going back to §2 it is seen that the average $\mathscr{A}$, in (29) and (30), which makes the medium isotropic leads to $K_{n+1} = 0$; then we finally obtain the result (31) which can now be seen to be the reduction to spherical tensor form of the susceptibility indicated in (A3.4).

Inspection of (31) for $n = 3$ shows that the only allowed values of (K_2, K_3, K_4) are $(0, 1, 0)$, $(1, 1, 0)$ and $(2, 1, 0)$—this agrees with the conclusion above that there are only three independent components of $\chi^{(3)}_{\mu\alpha_1\alpha_2\alpha_3}(+\omega_0; \omega_1, \omega_2, \omega_3)$.

The above argument needs modification for a gas of molecules which do not possess inversion symmetry. In this case $\mathscr{G} = \mathrm{R}^+(3)$, as the medium is isotropic, and so the identity is $D^{(0)}$. As the rotations $\mathrm{R} \in \mathrm{R}^+(3)$ are proper, the characters of $D^{(0)}_+$ and $D^{(0)}_-$ are the same for these R, and so tensors of all ranks are allowed. Hence in using the formulae presented here, in such cases we can remove the restriction on allowed orders of nonlinearity. It might be noted that for the second-order nonlinearity in optically active liquids (isotropic, but no centre of inversion) it can be concluded that

$$\boldsymbol{E}_{-\omega_0}.\boldsymbol{P}^{(2)}_{\omega_0} = -\frac{1}{\sqrt{3}}\epsilon_0\chi(K_2 = 1)^{(K_3=0)}_0(\boldsymbol{E}_{-\omega_0} \times \boldsymbol{E}_{\omega_1})^{(1)}.\boldsymbol{E}_{\omega_2}$$

using (21). As $(\boldsymbol{\epsilon}_1 \times \boldsymbol{\epsilon}_2)^{(1)} = \mathrm{i}(\boldsymbol{\epsilon}_1 \times \boldsymbol{\epsilon}_2)/\sqrt{2}$ and the dot and cross can be interchanged in a scalar vector triple product, we find

$$\boldsymbol{P}^{(2)}_{\omega_0} = -\frac{\mathrm{i}}{\sqrt{6}}\epsilon_0\chi(K_2 = 1)^{(K_3=0)}_0\boldsymbol{E}_{\omega_1} \times \boldsymbol{E}_{\omega_2}. \tag{A3.5}$$

This is exactly of the form obtained by Giordmaine (1965) after averaging over all proper rotations, in his discussion of second harmonic generation ($\omega_0 = 2\omega$, $\omega_1 = \omega_2 = \omega$) in optically active liquids.

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